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TO: Dr. D. Mills
Director of Research

NON-CONTACT THERMOMETRY BY LASER-INDUCED FLUORESCENCE OF SURFACE-BONDED PHOSPHORS

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The temperature of a surface can be determined by a non-contact method based on measurement of the decay time of the fluorescence stimulated in certain phosphors by ultraviolet light. The technique can be adapted to rotating surfaces and to measurements at a distance, while covering a temperature range of less than -60°C to greater than 1000°C depending on the choice of phosphor and emission wavelength. Potential applications are considered, with special emphasis on the temperature monitoring of the rotor in an electrical generator (80-150°C). Laboratory studies have identified the optimum phosphor for this particular application.

1. INTRODUCTION

One method of determining the temperature of an object is by measuring the intensity or decay time of the visible fluorescence emitted by a phosphor in thermal contact with the object following excitation by ultraviolet light. This has been the basis of commercial instrumentation developed by Luxtron over the past several years, in which a phosphor is bonded to the end of an optical fiber to form a small, electromagnetically inert temperature probe/1/. Luxtron has also done some research into non-contact thermometry using this approach. In this case a mixture of the phosphor and a suitable binder is painted on the surface and an open-ended optical fiber is used in place of the normal probe.

A much more extensive investigation of the non-contact approach has been carried out at Martin Marietta Energy Systems in Oak Ridge, with particular emphasis on rotating surfaces because the original stimulus for the research was the need for remote thermometry of the surfaces of rotors in gas centrifuge uranium

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isotope separation/2/. Among other things, the Oak Ridge research has demonstrated the wide temperature range that can be covered by remote phosphor thermometry, from room temperature to greater than 1000 °C. Other researchers have used the technique at temperatures as low as 77 K/8/.

Such a non-contact method of temperature measurement would appear to be a useful tool for a variety of electrical utility applications and some of these will be considered in this report. Of particular interest at the moment is the measurement of generator rotor temperatures as part of an EPRI-funded project dealing with the aging of rotating machinery insulation (ARMI). Since this application involves temperatures from 80°C to 150°C the laboratory studies presented in this report will emphasize this temperature range.

2. MEASUREMENT CONCEPT

Phosphors are solid materials which emit light when stimulated by sources of excitation such as electrons or light. This phenomenon is called luminescence and occurs in everyday applications such as television screens and fluorescent lamps. The emission of light is termed fluorescence if it is short-lived (<1 μs) and phosphorescence if it persists for >1 μs after the excitation source is removed. Usually a phosphor consists of an activator or impurity ion introduced into the host matrix at concentrations up to a few per cent.

In most cases the luminescence takes the form of broad band emissions but certain rare earth phosphors emit sharp lines in the visible when excited by ultraviolet light and both the intensity and decay time of the visible emission are dependent on the temperature. Over a certain range of temperatures, which depends on the host matrix as well as on the specific activator transition, the emission intensity and decay time fall sharply with increasing temperature. This thermal quenching originates in the competition between radiative and non-radiative transitions in the phosphor.

Figure 1 is a spectrum of one of these rare earth phosphors, europium-doped gadolinium oxysulfide ($Gd_2 O_2 S$:Eu), showing both the ultraviolet absorption, which extends from 200 to 400 nm, and the visible emission, which ranges from 460 to 630 nm. The emission lines are separated into three groups, labelled $^5D_2$, $^5D_1$ and $^5D_0$ according to the initial spectroscopic state of europium in the particular transition. Each of these three sets of lines yields a different temperature dependence. Normally a nitrogen laser at 337 nm is used to stimulate the phosphor and an interference filter is used to select the emission line which gives the desired temperature range.

An example of the range of temperatures that can be covered by a single phosphor is given in Figure 2 which shows the temperature dependence of the emission intensity for three sets of transitions in europium-doped lanthanum oxysulfide ($La_2 O_2 S$:Eu). Measuring the decay time of the emission yields a similar pattern, so that this particular phosphor represents a useful temperature sensor over the ranges 210 to 310 K (-63 to 37°C), 380 to 500 K (107 to 227°C), and above 500 K (227°C). Figure 2 also shows the effect of changing the host matrix on the $^5D_2$ transition. Similar changes would occur for the other transitions. From this it is apparent that a broad range of temperatures can be covered by a relatively small number of different phosphors, all of which could have the same europium activator and hence the same emission spectrum.

The detailed spectroscopy of these rare earth phosphors has been examined by researchers at RCA Laboratories who also succeeded in explaining the thermal quenching results using a model which focuses on crossings between the ^5D levels of the europium ion and charge transfer states whose energy levels depend on the host matrix/3,4/.

3. EXPERIMENTAL STUDIES

In applying the temperature sensitive phosphor to a particular surface there is a requirement for a binder which is both ultraviolet transparent and is able to withstand the maximum temperature of interest, which is 150°C in the case of rotor temperature monitoring. Most epoxies have a maximum operating temperature of 125°C so we chose to use silicone resin (Dow Corning 806 A) for this purpose. Laser absorption measurements confirmed that this material was virtually free of absorption at 337 nm.

Considerations of published thermal quenching data for rare earth phosphors indicate that there are two primary candidates for the 80 to 150°C range, $Gd_2 O_2 S$:Eu and $Y_2 O_2 S$:Eu. The former was purchased from Luxtron and the latter was obtained from Dr. W. Fonger of RCA Laboratories in Princeton N.J., who provided three samples with europium concentrations of 0.1%, 0.3% and 1%. Martin Marietta Energy Systems also provided a small sample of $La_2 O_2 S$:Eu which served as a benchmark to ensure that our measurements gave results consistent with those of the Oak Ridge group.

The experimental set-up used to measure the temperature dependence of the decay time for these phosphors is shown in Figure 3. The Quantel Nd:YAG pumped dye laser was tuned to 337 nm using oxazine 720 dye and frequency doubling the output at 674 nm. This wavelength was chosen to simulate the output of a compact

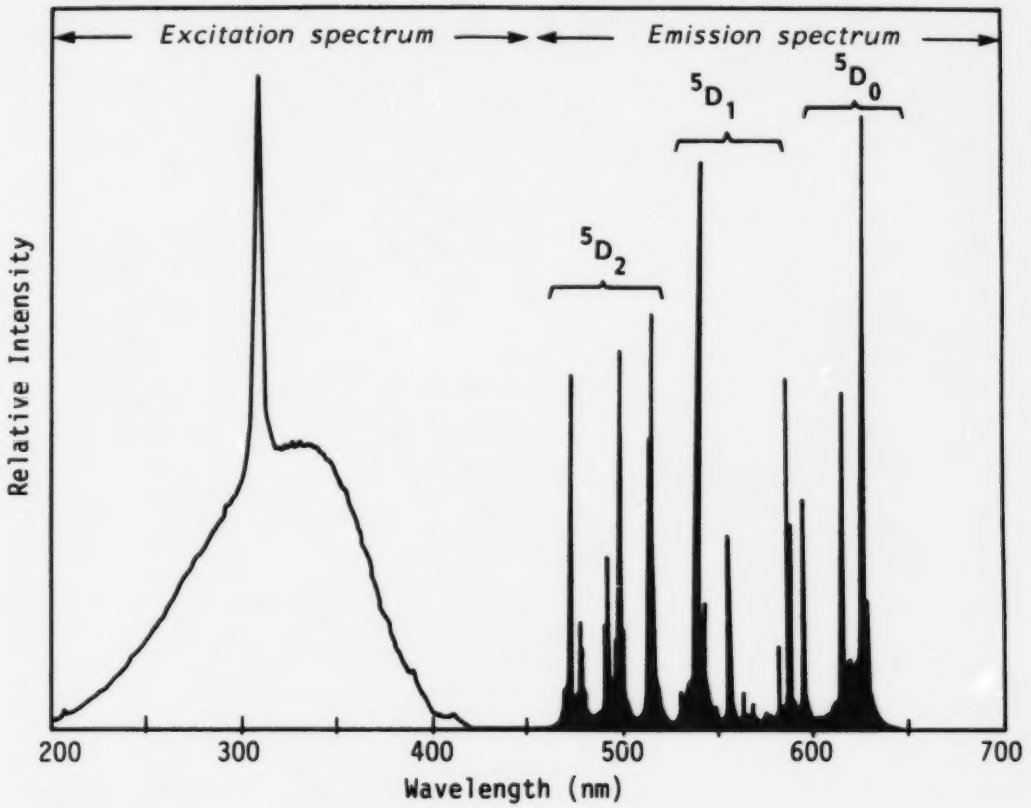

FIGURE 1

EXCITATION AND EMISSION SPECTRA OF
EUROPIUM-DOPED GADOLINIUM OXYSULFIDE

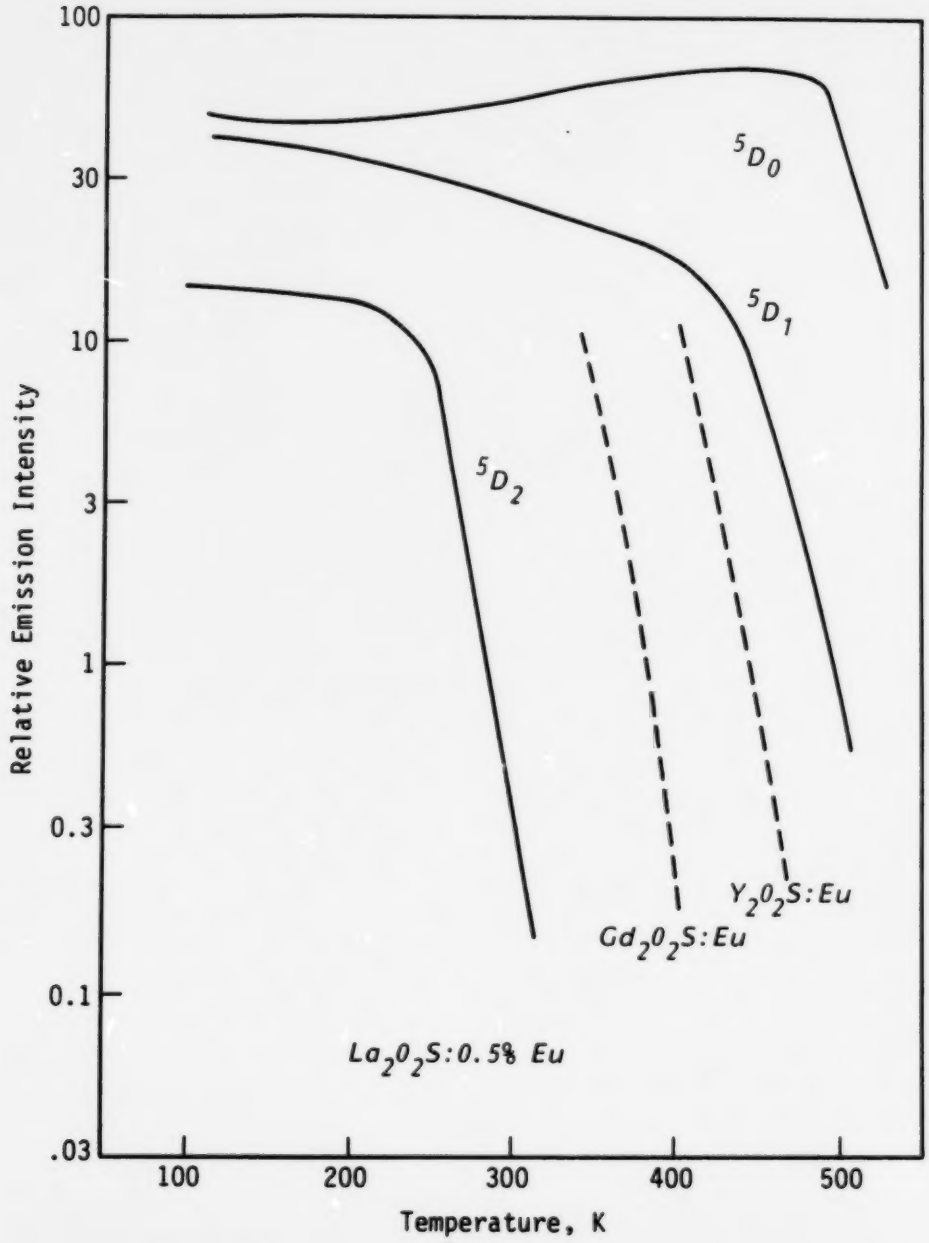

FIGURE 2

TEMPERATURE DEPENDENCE OF ^5D EMISSION IN EUROPIUM-DOPED LANTHANUM OXYSULFIDE. THE DASHED LINES INDICATE THE EFFECT ON $^5D_2$ OF CHANGING THE HOST TO GADOLINIUM AND YTTRIUM OXYSULFIDE.

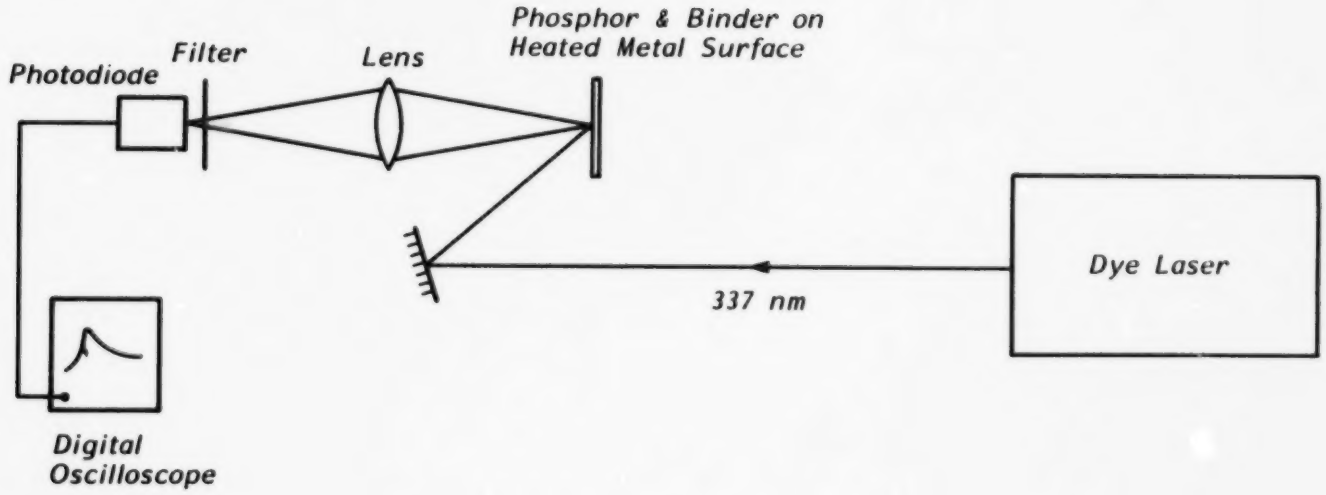

FIGURE 3

SCHEMATIC OF EXPERIMENTAL SET-UP
TO MEASURE TEMPERATURE DEPENDENCE OF PHOSPHOR DECAY TIME

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later use in this application. Various glass filters were used to vary the output energy from 1 mJ to 50 μJ.

A 1:1 mixture of phosphor and binder was applied to the surface of a piece of aluminum in contact with a temperature controlled surface whose temperature was monitored with a thermocouple.

The visible emission resulting from the ultraviolet excitation of the phosphor was filtered at 514 ± 5 nm to isolate the $^5D_2$ line which actually consists of a triplet as revealed by high resolution spectroscopy. Signal detection was accomplished with a fast photodiode (1 μs response time) connected to a Biomation Model 4500 digital oscilloscope.

4. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4 shows a typical decay curve as measured for Y_2O_2S:1% Eu phosphor at 129.5°C using 0.4 mJ of 337 nm excitation. The decay is approximately exponential and the decay time, defined as the time for the signal to fall by a factor 1/e, is 4.48 μs in this example.

Measurements of the decay time of the 514 nm triplet as a function of temperature for the La_2O_2S:Eu phosphor gave results similar to those at Oak Ridge, namely a strong dependence over the range 20°C to 60°C/2/. As noted earlier in the discussion of Figure 2, the $^5D_2$ transition of this phosphor at 514 nm can serve as a temperature monitor all the way down to -63°C. Using a different emission line at 540 nm ($^5D_1$ transition) resulted in quenching from 150°C to 210°C, as expected from Figure 2.

A more detailed temperature study was performed with the 514 nm triplet of the Gd_2O_2S:Eu phosphor, with the results shown in Figure 5. The exponential relationship between decay time and temperature is demonstrated by the straight line obtained when the data are plotted on a semi-logarithmic graph. Theoretical considerations/5/ give the dependence of phosphor emission intensity I on time t by:

$$I(t) = I(o)\ \exp(-\alpha t) \qquad (1)$$

where α is the decay constant, equal to the inverse of the decay time τ as defined above. The dependence of α on the absolute temperature T is given by:

$$\alpha = \frac{1}{\tau} = A\ \exp(-\epsilon/kT) \qquad (2)$$

where A and ε are constants and k is Boltzmann's constant. The constant ε is an activation energy which is equal to the thermal barrier for the quenching process.

Equation (2) predicts a linear relationship between ln τ and T^{-1}, which is verified by re-plotting the experimental data as shown in Figure 6. In both Figures 5 and 6 the straight lines result from a least squares regression analysis of the data.

Similar measurements were performed on the 514 nm triplet in Y_2O_2S:Eu phosphors, with the data for the case of 1% europium doping shown in Figure 7. The results are similar to those obtained with the Gd_2O_2S:Eu phosphor except that the decay time is greater at a particular temperature, by factors ranging from 2 at 70°C to 3.5 at 120°C. Further details of the results with Y_2O_2S:Eu phosphor and the reasons for the selection of the 1% doped version as the optimum choice for the 80-150°C range can be found in the Appendix.

We have not performed a detailed study of the accuracy of the remote phosphor technique but, judging from the data of Figures 5 and 7, we can estimate an uncertainty ±1°C for temperatures in the neighborhood of 100°C. Martin Marietta performed repeated measurements near 35°C and concluded that the uncertainty was ±0.3°C/7/.

5. POTENTIAL APPLICATIONS

As demonstrated by the research at Martin Marietta/2/, remote phosphor thermometry can be applied to rotating machinery by using the laser as a stroboscope to view the same spot on the rotating surface during each pulse. This approach can be used to monitor the temperature of the rotor in an electrical generator/1/. The normal operating temperature of the rotor is 80 to 90°C but in the middle section temperatures can be 30 to 40°C higher, based on manufacturers' design data, due to the cooling gas being discharged in this region after picking up heat from the rotor windings. There is an interest in measuring the extent of this "temperature bump". It may also be possible to measure rotor winding temperatures directly using certain balancing holes in the rotor wedges, thereby enabling the detection of hot spots in the rotor insulation/6/. This is the area of interest for the ARMI project referred to in the introduction.

Overheating of the rotor wedges, which are used to prevent movement of the rotor windings during operation, can lead to creep fracture. In certain situations this results in wedge replacement after 8 or 9 years, an expense which could be avoided or at least delayed if a temperature monitoring system were in place.

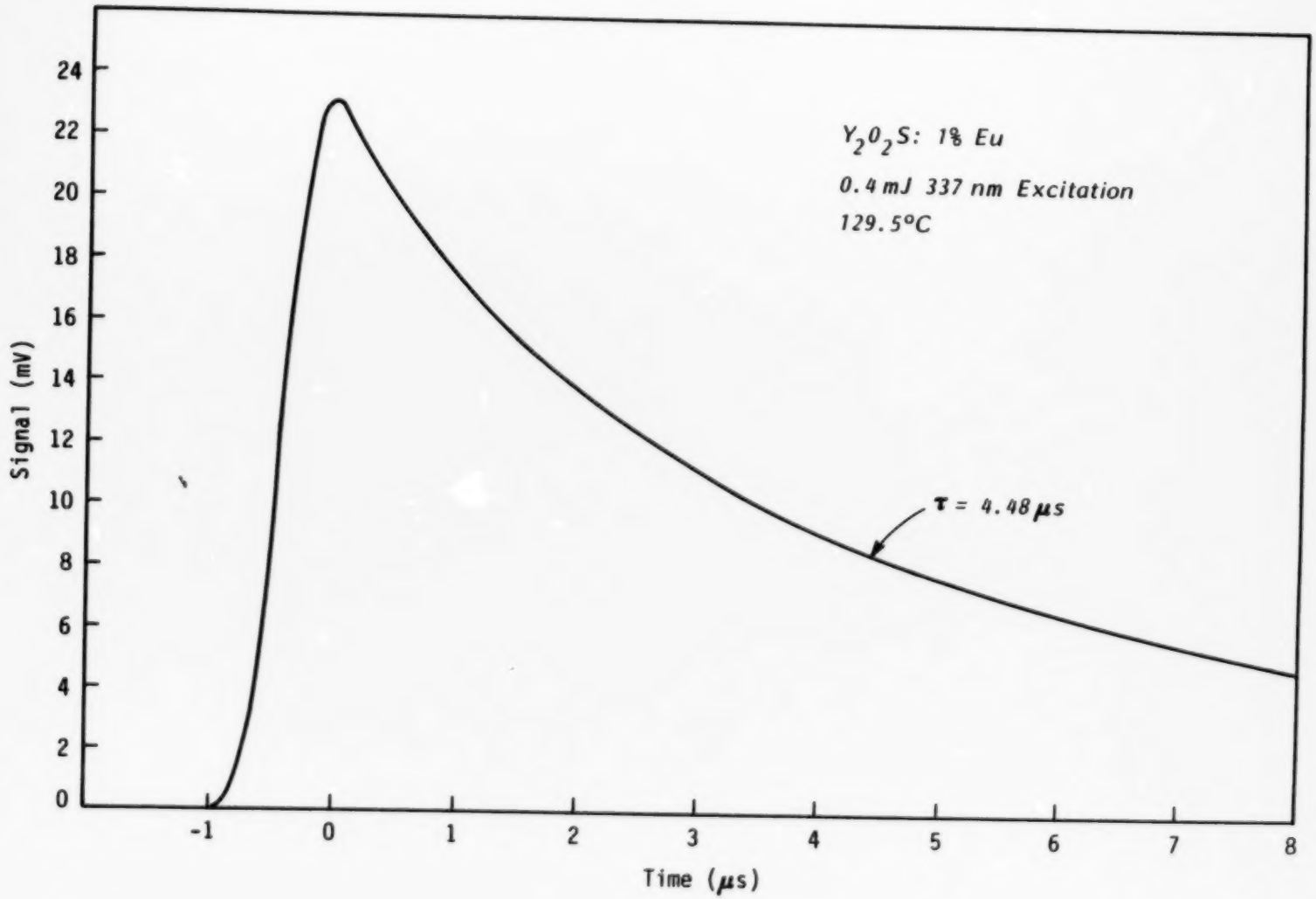

FIGURE 4

EXPONENTIAL DECAY OF PHOSPHOR EMISSION
AS MEASURED BY DIGITAL OSCILLOSCOPE

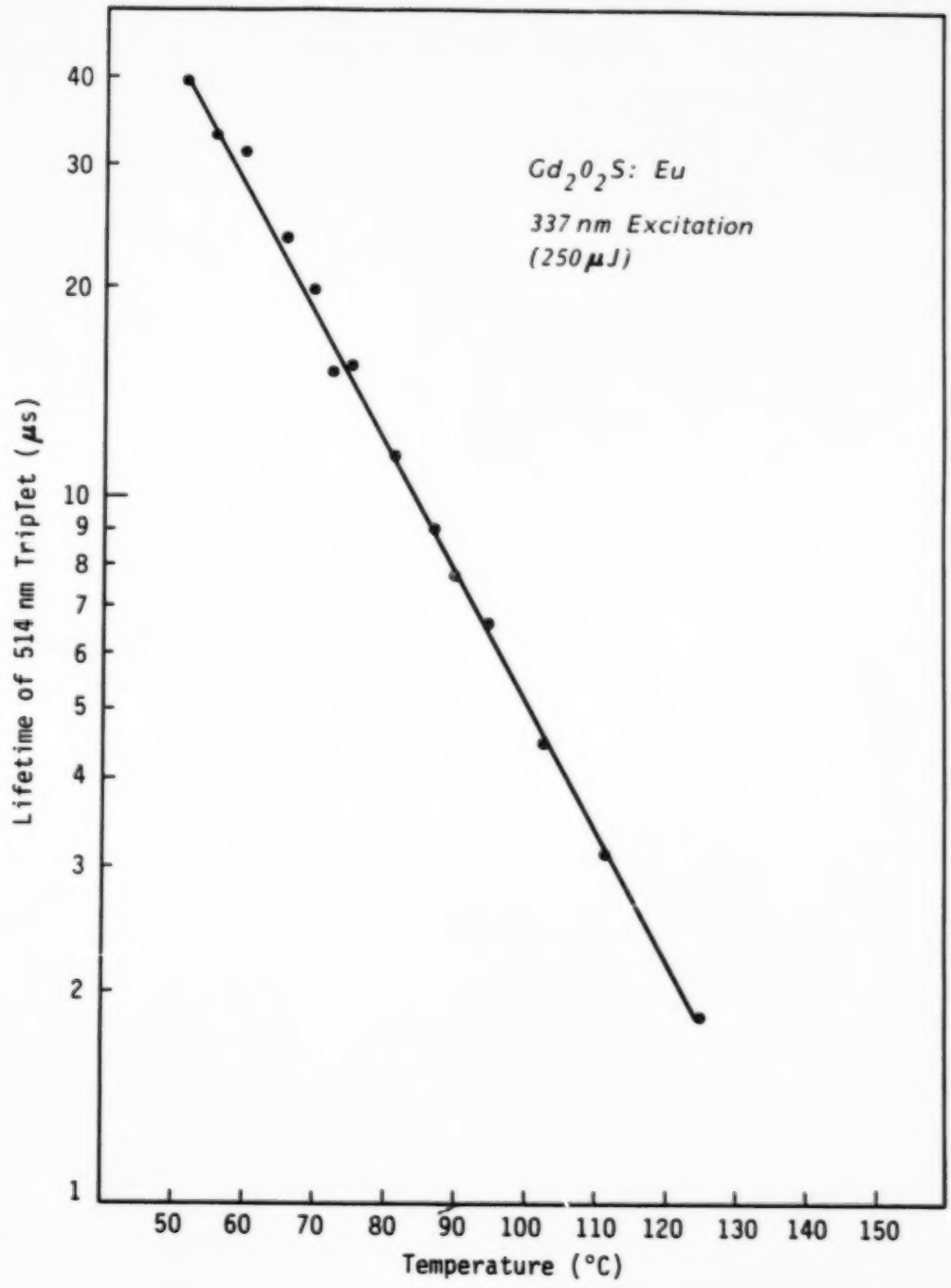

FIGURE 5

TEMPERATURE DEPENDENCE OF LIFETIME OF 514 nm EMISSION IN EUROPIUM-DOPED GADOLINIUM OXYSULFIDE

Both of these generator applications would depend on finding a method of stringing an optical fiber through the machine to deliver the light beams to and from the phosphors painted on the rotor surface. Obviously such an installation could only be carried out during an outage when the rotor was removed from the generator.

Other potential applications that have come to light as a result of discussions with Research Division personnel include hot spot detection in transformer bushings (80-120°C), surface temperature measurements of pressure tubes in laboratory studies (180-300°C) and temperature monitoring of insulators during icing studies (-5°C and higher). In some cases these involve measurements at distances of several meters or more and therefore either an optical fiber or a telescope would be needed to deliver the phosphor emission to the detector.

It should be noted that some of these applications may be handled by recently developed commercial instrumentation, such as the Luxtron Model 750 Fluoroptic Thermometry System described in Reference 1, which is also based on phosphor decay time measurements but which uses a different type of phosphor. However, there is still no commercial equipment capable of measurements on rotating surfaces and it is also worth noting that previous versions of fluoroptic thermometers have suffered from reliability and durability problems. It remains to be determined whether or not the latest models represent a significant improvement in the technology of remote non-contact temperature sensing.

6. CONCLUSIONS

1. Measurement of the decay time of the luminescence induced in certain rare earth phosphors by ultraviolet light represents a non-contact method of measuring surface temperatures.

2. The technique can be adapted to rotating surfaces and can also be used in measurements at a distance by adding an optical fiber or a telescope.

3. Temperatures ranging from less than -60°C to greater than 1000°C can be covered by a suitable choice of phosphor and emission wavelength.

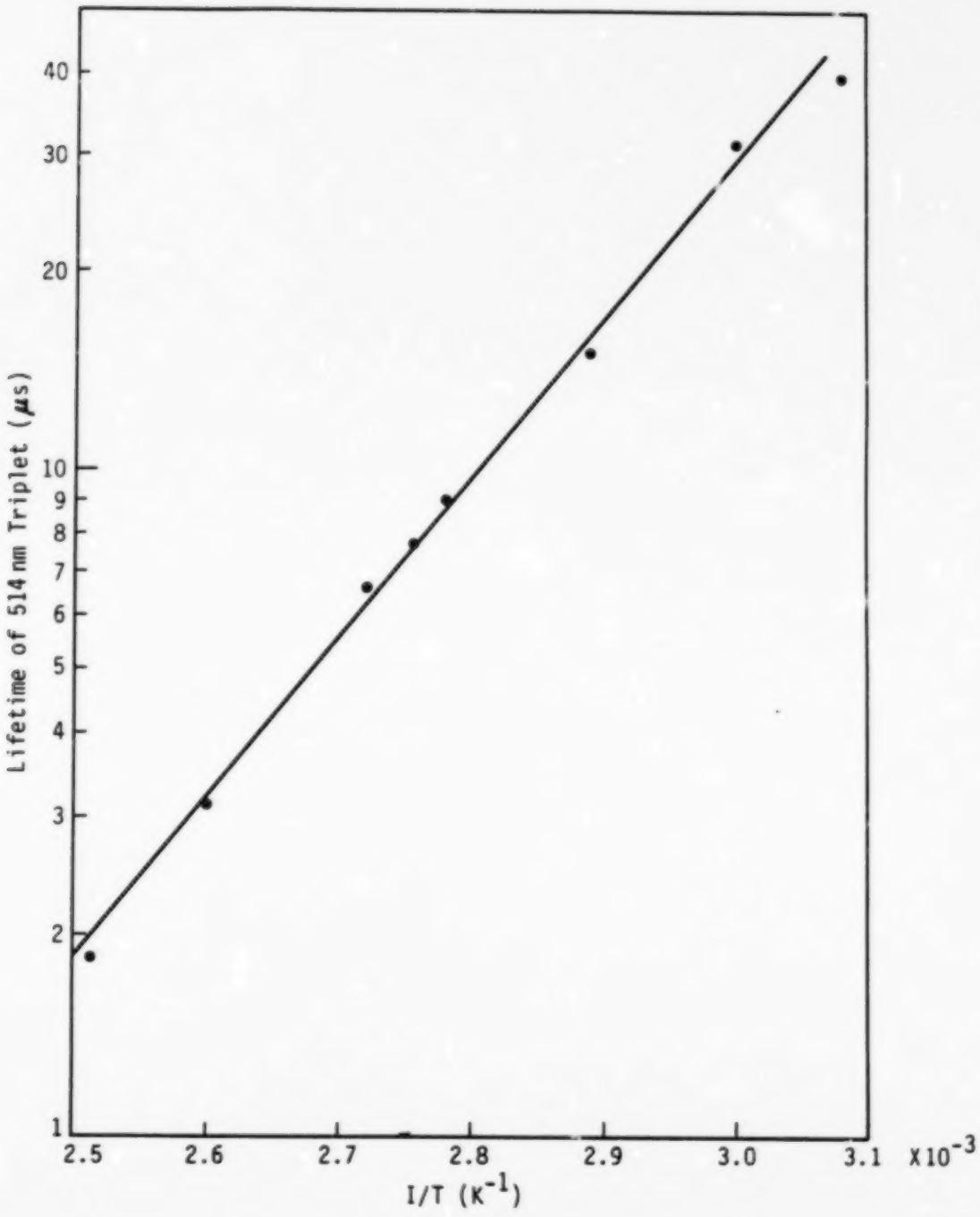

FIGURE 6

PLOT OF PHOSPHOR DECAY TIME AGAINST INVERSE OF THE ABSOLUTE TEMPERATURE FOR 514 nm EMISSION IN EUROPIUM-DOPED GADOLINIUM OXYSULFIDE

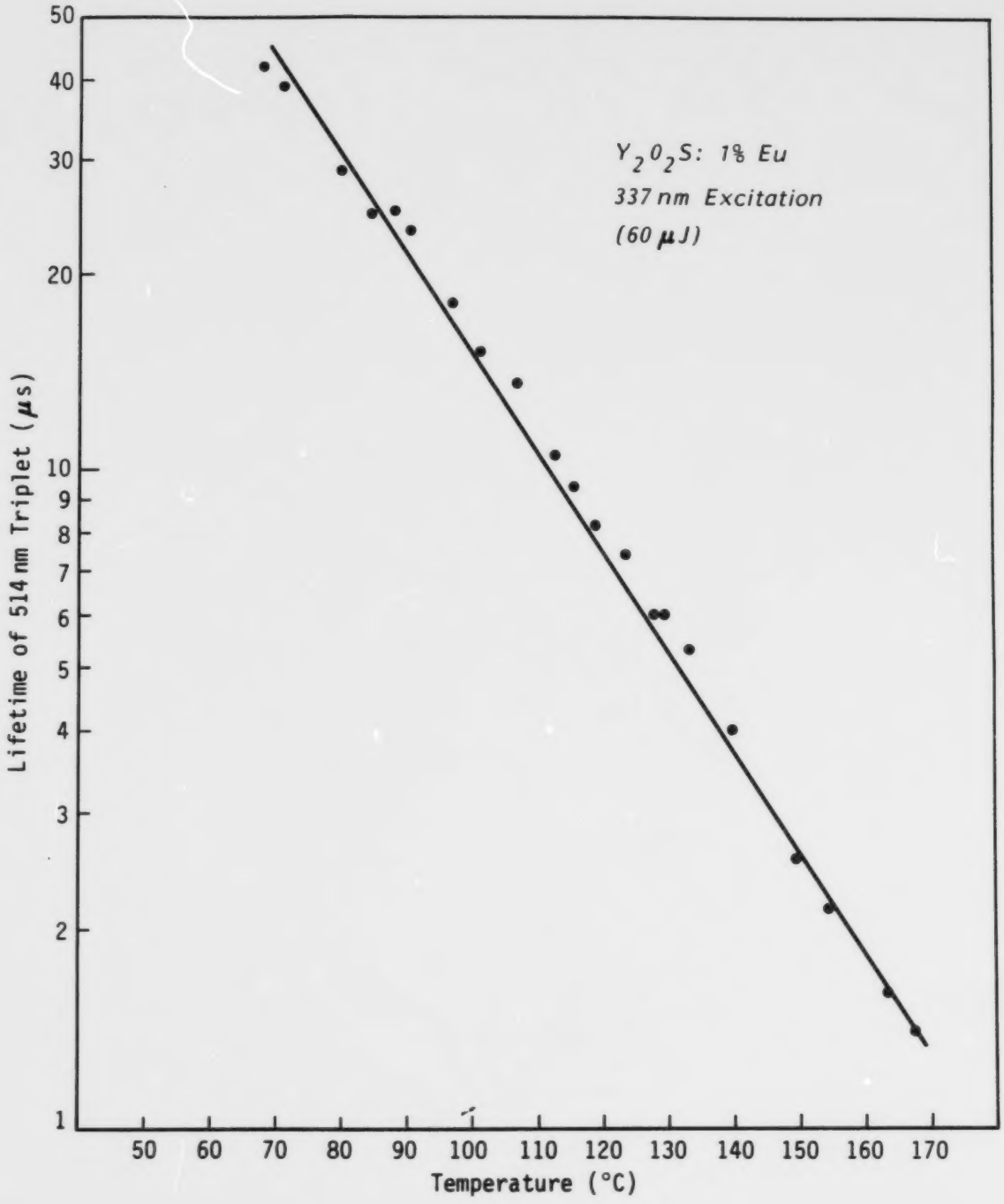

FIGURE 7

TEMPERATURE DEPENDENCE OF LIFETIME OF 514 nm EMISSION IN EUROPIUM-DOPED YTTRIUM OXYSULFIDE

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4. The phosphor of choice for the temperature range 60 to 150°C is yttrium oxysulfide doped with 1% europium.

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APPENDIX

SELECTION OF Y_2O_2S:1% Eu AS THE OPTIMUM PHOSPHOR FOR 80-150°C

One of the criteria for selecting the optimum phosphor for a particular temperature range is that at the highest temperature the decay time is long enough to be accurately measurable given the response time of the detector. On this basis the Y_2O_2S:Eu phosphor is preferred over the Gd_2O_2S:Eu for the 80 to 150°C range because with the former the decay time at 150°C (2.5 μs) can be measured with the 1 μs detector while with the latter the decay time at this temperature is too small (cf Figures 5 and 7). Reducing the response time of the detector can be achieved by lowering the resistance of the external circuit connected to the photodiode and using an amplifier to overcome the resulting reduction in sensitivity. This approach will be used in future experiments to extend the temperature range of the Y_2O_2S:Eu phosphor.

The 0.1% and 0.3% europium doped Y_2O_2S phosphors yielded higher decay times for a given temperature. However, these phosphors suffered from a problem not apparent with the 1% doped phosphor, namely the appearance of a spike at the beginning of the decay curve, as seen in Figure 8. While this spike could be ignored at lower temperatures where the decay was slow enough to make it readily distinguishable from the phosphor decay, this was not the case at higher temperatures where the spike blended in with the main phosphor decay curve and led to spurious measurements of decay time.

We ascribe this effect to an impurity formed by a chemical reaction between the binder and phosphor, which yields a broad band fluorescence, part of which is transmitted by the 514 nm filter. Similar spiking is observed when any fluorescing material such as plastic or paper is placed in the laser beam. Interestingly, the spike is absent when the binder and phosphor are first mixed and appears only during the curing process. It is also absent with the phosphor or binder alone. Presumably the reason this phenomenon is not observed at the highest europium concentration

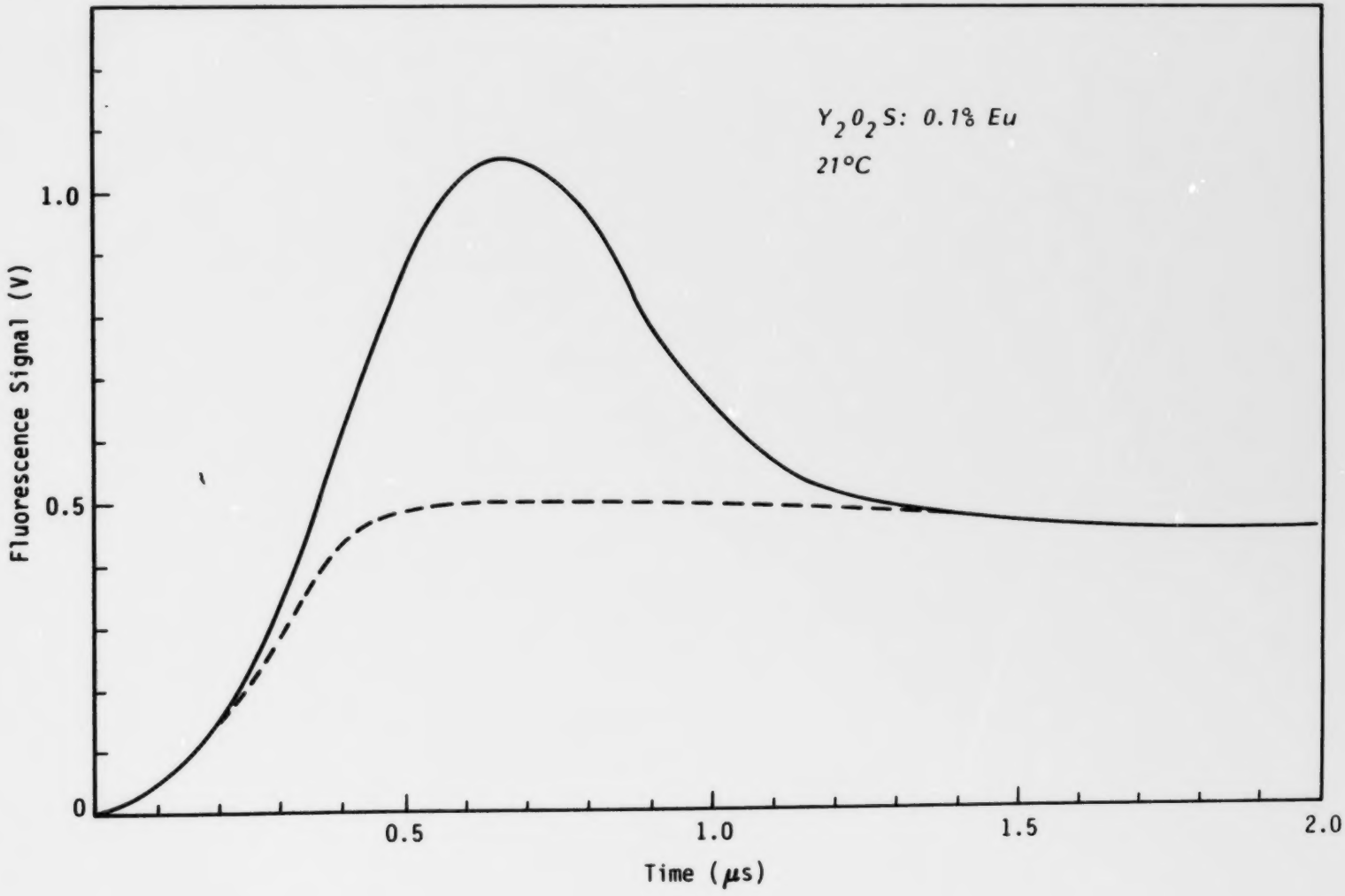

FIGURE 8

PHOSPHOR DECAY CURVE FOR 0.1% EUROPIUM-DOPED YTTRIUM OXYSULFIDE
SHOWING A <1 μs SPIKE DUE TO IMPURITY FLUORESCENCE.
THE DASHED CURVE REPRESENTS THE EXPECTED TIME DEPENDENCE WITHOUT SPIKING.

is that in this situation the normal phosphorescence associated with the phosphor is so intense that it masks the impurity fluorescence. For the same reason the effect is less noticeable in thicker samples.

Another effect first observed with the $Y_2 O_2 S$ samples is that the decay time depends on the energy of the exciting laser beam. This would place serious limitations on the applicability of this technique since dust or other impurities depositing on the optics or the phosphor/binder surface would reduce the ultraviolet energy reaching the phosphor in an unpredictable manner. Fortunately, there exists a threshold energy value below which the decay time is independent of the laser energy. Detailed measurements with the $Y_2 O_2 S$:1% Eu phosphor gave a threshold energy of 100 μJ. This saturation effect has been observed by other researchers studying this phosphor/8/ and an explanation has been proposed based on the interaction between excited europium ions.